X-Ray Emission Spectra and Electronic Energy Bands of Compounds

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Measurements of emission wave-lengths in the $K\beta$ group of Ca and S in CaS and $CaSO_4$, of Mg and S in MgS, of S in SrS and BaS, of Ca and Cl in $CaCl_2$ have been made from the secondary radiation from pressed blocks of the salts. An attempt is made to determine the origin of as many x-ray lines as possible by means of electronic energy band systems in the cases of CaS, MgS, and ZnS. The $K\beta_5$ line of Zn in ZnS and the $K\beta_1$ line of Mg in MgS are found to be due to cross transitions from the outermost filled band of the negative ion.

IT has been pointed out that information in regard to electronic energy bands in solids may be obtained by a study of x-ray emission[1] and absorption[2] spectra. In the second paper of reference 1, it is shown that the principal lines in the x-ray emission spectra of alkali halides fit the energy level diagrams for the solid state with fair accuracy, leaving no doubt as to the levels and transitions which account for some of these lines. However, there are still several prominent lines which cannot be accounted for with certainty. The present paper summarizes recent measurements of wave-lengths in the $K\beta$-radiation from alkaline earth sulphides and a few other compounds. The discussion reveals anomalies which were absent in the spectra of the alkali halides.

The radiation was excited by placing pressed blocks of the compound near the focal spot on a tungsten-surfaced anticathode as described in a previous article.[3] An attempt was made at this time to record as many of the satellites of $K\beta_1$ as possible with this indirect method of excitation. A Siegbahn vacuum spectrograph equipped with a quartz crystal was employed. The power input to the tube was kept low enough so that the material did not show any appreciable alteration. However, the material was changed every 24 hours during the exposures, which ranged from 100 to 500 hours. The power input was 1 to 3 ma at 12 kv depending on the stability of the substance.

For the Mg $K\beta_1$ line a focusing spectrograph with a curved mica crystal was employed. The radiation was from a pressed block of MgS which received radiation from an adjacent tungsten plate which was bombarded by electrons. The wave-length was measured relative to that of copper $K\alpha_1$ in the eighth and tenth orders as well as Al $K\alpha$ in the second order.

In the other cases, the wave-lengths were measured relative to those previously given for the principal $K\beta_1$ lines[1] from the same compounds. The line intervals were measured with a Gaertner comparator. Each spectrogram contained a number of lines which were too weak

[1] J. Valasek, Phys. Rev. 51, 832 (1937); Phys. Rev. 53, 274 (1938).

[2] R. Landshoff, Rev. Sci. Inst. 9, 143 (1938); Phys. Rev. 55, 631 (1939).

[3] J. Valasek, Phys. Rev. 47, 896 (1935).

to measure directly since they disappeared into the granular background even under low magnification. When microphotometer traces were made of these lines, it was found difficult to locate accurately the exact maximum because of the line breadth and the accidental irregularities in the trace. It was found just as accurate to mark carefully the location of the line on the plate with a sharp pencil and to measure the mark. Repetition of this procedure on the same and on different plates gave results which were usually consistent to about 1 X.U. and the average should be good to about 0.5 X.U. as a rule. These lines are designated by b in Table I. The lines designated by a were always measured directly and are probably correct to 0.1 X.U. in general.

The auxiliary data needed to assist in the interpretation of the lines are most complete in the case of CaS. In Fig. 1, the emission lines of Ca and S are plotted on a scale of electron volts below the K-absorption edge for the corresponding element. The wave-length of the K edge of S in CaS, 5006.6 X.U., was obtained from the measurements of Lindh.[4] That for the K edge of Ca in CaS, 3059.5 X.U., was obtained by applying a correction to the measurements of Aoyama, Kimura, and Nishina.[5] These authors as well as Lindsay and Van Dyke[6] have measured

the K-absorption wave-lengths of Ca in various compounds. There is an average difference of 3.1 X.U. between the two sets of measurements on the same compound, although Lindsay and Van Dyke give no values for CaS. The difference between the two groups of observers is largely due to the fact that the former measured the middle of the first white line in the absorption spectrum, while Lindsay and Van Dyke measured the beginning of absorption. In view of both sets of data, it is considered that the most probable value of the K-absorption edge of Ca in CaS is determined by the most rapid rise in absorption which is estimated to be 1.6 X.U. above the value given by Aoyama, Kimura, and Nishina, namely at 3059.5 X.U.

In order to fit the energy levels of both ions to the same energy scale, it will be assumed at first that the K electron, at the beginning of the continuous K absorption, is raised to the lower edge of the same band of empty states of the crystal lattice regardless of whether it comes from the K shell of the positive or the negative ion. Accordingly, when they are both known, the absorption edges of both ions are placed at the same point in the energy level diagram. The locations of the emission lines should then show the locations of the initial occupied level from which the emitting electron falls into the K shell. This assumes a single excitation and a single electron transition, and hence does not apply to the spark lines.

In the cases of NaCl and KCl reported in a previous article, the origin of four of the emission lines was plainly indicated when a diagram prepared as above was compared with an energy level diagram prepared from the atomic levels by the method of Slater and Shockley.[7] Two of these lines were, as expected, due to transitions of a $3p$ electron into a K shell vacancy in the same ion, while two were due to transitions of a $3p$ electron into a K shell vacancy in a neighboring ion of opposite sign. The latter are usually much weaker than the former except when the $3p$, or sometimes the $2p$, shell is not occupied in one of the ions because of its low atomic number. Then the cross transitions give rise to principal lines. Further evidence on this point is presented below.

TABLE I. *Wave-lengths in X.U.*

LINE TYPE		WAVE-LENGTHS					
		Negative ion, S⁻⁻ (and Cl⁻)					
		MgS	CaS	SrS	BaS	CaSO₄	CaCl₂
	b	5124.3	5083.5	5084.4	5093.4	5087.1	
β_4	b	5067.3	5065.3	5065.3	5067.1	5067.3	
β_3	b	5046.2	5046.2	5046.4	5044.3	5046.2	4419.6
β_1	std	5018.40	5019.00	5019.39	5019.74	5017.81	4394.61
β_x	a	5011.9	5012.6	5012.3	5012.4	5011.1	4380.9
β_6	b	4993.5	4993.6	4994.0	4994.2	4990.1	4368.9
β'''	b	4950.0	4950.6	4951.2	4954.6	4951.6	
β''''	b	4933.3	4934.0	4934.3	4931.1	4933.1	
	b	4889.0	4891.3	4885.5	4891.6	4896.7	
	b	4862.5	4871.6	4871.5	4866.0	4865.1	
	b					4970.8	

		Positive ion, Ca⁺⁺ (and Mg⁺⁺)				
		CaS	CaSO₄	CaCl₂		MgS
η	b	3122.	3122.	3125.		
β'	b	3111.	3110.	3114.		
β_1	std	3083.43	3083.43	3083.43	β_1 a	9545.
β''	a	3079.2	3079.3	3079.3		
β_5	a	3067.3	3068.1	3068.1		
β'''	b	3048.3	3048.1	3048.1		
β''''	b	3041.3	3042.7	3041.2		

[4] A. Lindh, Handb. d. Exp. Physik, Vol. 24, No. 2, p. 296.
[5] S. Aoyama, K. Kimura, and Y. Nishina, Zeits. f. Physik 44, 810 (1927).
[6] G. Lindsay, and G. Van Dyke, Phys. Rev. 28, 613 (1926).
[7] J. Slater and W. Shockley, Phys. Rev. 50, 705 (1936).

Because the alkaline earth sulphides also have a rocksalt type of structure, one can readily apply the same calculations to find the locations of their energy bands for the purpose of comparison with similar results obtained from the x-ray data. Because of the double charge on each ion, the electrostatic potential energy term must be multiplied by two. Accordingly

$$e\phi = \frac{3.495 \ e^2 \ 300}{r} \text{ electron volts,}$$

where r is the distance between closest neighbors of opposite sign. The ionization potential, or electron affinity, of the S^{--} ion is calculated by extrapolating the ionization potentials of the isoelectronic sequence Ca^{++}, K^+, A, Cl^- by means of a quadratic formula.[8] The potentials used are taken from Bacher and Goudsmit's *Atomic Energy States*. The work required to remove one electron from S^{--} is thus found to be -4.18 electron volts. Seitz[9] has recently used a value of -5 volts which he obtained by subtracting an estimated binding energy for the first electron from the electron affinity found by the use of a Born cycle. The cycle gives the work done to remove both electrons. The negative sign applied to the electron affinity indicates that the free doubly charged ion is unstable. In a crystal lattice, however, more than enough binding energy is supplied through the external screening by surrounding ions to result in a positive binding energy of some 10 to 15 electron volts, depending on the compound.

The ionization potentials for the doubly charged positive ions of Mg and Ca are also from Bacher and Goudsmit's tables. However those for Sr^{++} and Ba^{++} are not listed, and since the K-absorption edges of these ions in the corresponding sulphides are also unknown, they are omitted from the following discussion.

Calculated positions of the energy bands for CaS are shown in Fig. 1. It is difficult to determine the extent of the continuum of empty states, but the experimental data can be used to supply this information. In order to do this, it is assumed that the intervals between the occupied energy bands of the positive ion are
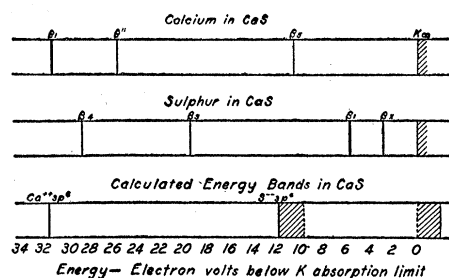
[8] G. Glockler, Phys. Rev. **46**, 111 (1934).

[9] F. Seitz, J. Chem. Phys. **6**, 454 (1938).

FIG. 1. Top: K-series emission lines of calcium in CaS on energy scale relative to the K-absorption edge. Center: ditto, sulphur in CaS. Bottom: electron energy bands of CaS.

not altered by chemical combination. This is indicated by the exceedingly small effects of such combination on the emission wave-lengths of the positive ion. Hence, if the $3p$ level of Ca is placed at the same point on the energy scale as the $K\beta_1$ line, the location of the K-absorption edge will give the location of the lower edge of the empty states in the compound. The other K lines should then indicate the upper filled states from which they originate. The Ca $K\beta_5$ line is thus seen to be due to a cross transition of an S $3p$ electron into the vacancy in the K shell of Ca.

However, it is evident on Fig. 1 that the placing of the K-absorption edge of the negative ion in coincidence with that of the positive ion, results in a large discrepancy in the location of the S $K\beta_1$ line with respect to the S $3p$ band. It should be noted that this displacement did not occur as a result of the application of the same considerations to the spectra of NaCl and KCl in an earlier article.[1] Obviously, one can remove the discrepancy in this case by an appropriate shift in the position of the empty states belonging to the sulphur ion. This would require a displacement of 5 to 7 electron volts with selection rules to reserve the shifted states for the negative ion. The existence of two such empty bands "belonging" to the respective ions does not seem improbable, for an examination of the wave-mechanical problem leads to a result of this general nature. When K excitation of the positive ion takes place, the K electron goes into a band derived from the lowest vacant p state of the positive ion. On the other hand when the K excitation of S^{--} takes place, the electron probably goes over into the vicinity of one of

the neighboring Ca^{++} ions. This is essentially the same state of Ca, but modified by the fact that the net charge on the ion core is one unit less. An application of Moseley's law as a first approximation gives much too small a displacement of the upper level to account for that observed. Thus it seems necessary to assume a great distortion of the outer levels of the negative ion either as a result of the nature of the chemical bond, or as a result of some secondary process which occurs between excitation and emission.

The first interpretation is ruled out because the cross-transition line $K\beta_5$ of Ca shows that the initial level S^{--} $3p$ is in its normal state when it is the positive ion which is excited. This conclusion is supported by similar lines in the spectra of MgS and ZnS as will be shown in the following. Thus the displacement of the S^{--} $3p$ level accompanies only the K excitation of the S ion itself and, by the Franck-Condon principle, should follow the excitation. Accordingly, the K-absorption frequency of S^{--} will be at its expected place in the compound but its $K\beta$-emission line will be displaced.

Following Gurney, one may assume two principal sources of such secondary effects on the energy levels, namely the displacement of surrounding ions and polarization. The net effect is to elevate the energy levels of the electrons in the K-excited ion whether it is positive or negative, that is to say, to decrease the binding energy. Aoyama, Kimura, and Nishina[5] have calculated the energy u_2 of rearrangement of surrounding ions when the central ion loses an electron. They used this as one of the terms in their explanation of the effect of chemical combination on absorption frequencies. Pauling[10] points out that this is incorrect because the rearrangement cannot take place during absorption, but must follow after it, and he substitutes an electron affinity of the crystal which he obtains from the diamagnetic susceptibility of the compound.

Aoyama, Kimura, and Nishina find that the energy u_2 is only 1 electron volt in the case of chlorine in sodium and potassium chloride, but becomes 10 electron volts in the case of sulphur in CaS, and 11 electron volts for sulphur in

MgS and ZnS. Furthermore, it is very small in the cases of the positive ions in all these substances. From the manner in which u_2 is calculated, this energy includes energy of polarization as well as displacement, though the former is not mentioned in the original article. It is questionable whether the lifetime of the K-excited states is large enough to permit ion displacements, but polarization should be considered and it is estimated that this will lead to a displacement of the valence levels of the central ion by some 5 to 6 electron volts. The discussion by Aoyama, Kimura, and Nishina shows that a similar effect escapes notice in the alkali halides and in the spectra of positive ions in general, because u_2 is relatively small in these cases.

A further indication that the energy levels of the negative ion can be shifted by several electron volts as a result of changes in the internal and external screening, is shown by the spectra of sulphur in the sulphates as compared with the corresponding sulphides.[1] The K-absorption edge of sulphur is found to be displaced toward higher energy values by 9.5 electron volts on the average. The $K\alpha$ lines are displaced to higher frequencies by 1.7 volts, showing that the L levels are also displaced considerably, the shift being 7.8 electron volts. On the other hand, the $K\beta$ lines are displaced by only 0.5 volt on the average. This shows an unusually large amount of distortion or relative displacement of the energy levels.

The above considerations show that energy level displacements of the indicated value can occur when the region around a sulphur ion is made more negative. The principal displacement applies to all levels equally, like the crystal potential effect previously considered. However a secondary effect of opposite sign applies principally to the outermost levels and makes for a decrease in binding. This differential shift takes place between excitation of the negative ion and emission by the same ion and is negligible in the case of the positive ion. Any influence which acts equally on the M and K levels cannot explain the effects of chemical combination on the observed emission wave-lengths. It is just this point which makes it difficult to calculate the exact magnitude of the effect beyond the rough approximation discussed above. One might ex-
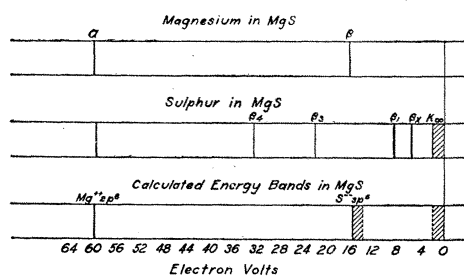
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[10] L. Pauling, Phys. Rev. **34**, 954 (1929).

FIG. 2. Top: K-series emission lines of Mg in MgS on energy scale. Center: ditto, sulphur in MgS showing relative location of K-absorption edge. Bottom: electron energy bands of MgS.
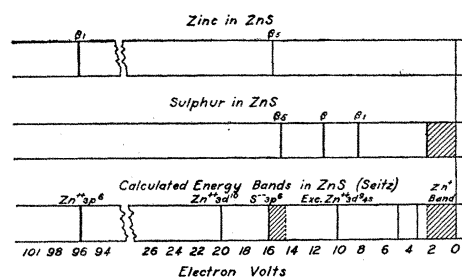

FIG. 3. Top: K-series emission lines of zinc in ZnS on energy scale. Center: ditto, sulphur in ZnS showing relative location of K-absorption edge. Bottom: electron energy bands of ZnS according to Seitz.

pect that it would increase with the polarizability of the ion concerned and the valence of the surrounding ions and their proximity. This is in accord with the observations, for the effects are greatest in the doubly charged negative ion in a divalent lattice with small lattice constant.

In the case of the spectrum of MgS, the wavelength of the K-absorption edge of Mg in the compound is not known, making it impossible to link together the spectra of S^{--} and Mg^{++} by making the vacant bands coincide as was done in the case of CaS. However, the locations of the energy levels in the crystal can be estimated as before by applying the crystal potential term to the levels for the free ion. The lower limit of the continuum of vacant states can be estimated to lie at about 2 electron volts by analogy with CaS, or by calculating the average energy of a free electron in the crystal from a formula given by Pauling.[10] Figure 2 shows the resulting diagram. The K edge of sulphur is made to coincide with the lower limit of the continuum and the magnesium $K\alpha$ line is placed opposite the Mg^{++} $2p$ level. There is no $3p$ level in a free magnesium ion from which a $K\beta$ line might originate. Nevertheless such a line is observed. Its location in the energy level diagram shows that it must be interpreted as a cross transition from the S^{--} $3p$ band. The same interpretation applies to the $K\beta_1$ line of Na in NaCl. The displacement of the S $K\beta_1$ line with respect to the parent S^{--} $3p$ energy band is about 6 electron volts which is in concordance with the result noted for CaS.

Recently F. Seitz[9] has published an energy level diagram for ZnS which is reproduced in

Fig. 3 with x-ray emission data for Zn[11] and S[12] in the same compound. The K-absorption edge of S in ZnS is taken from the tabulation by Lindh, but the wave-length of the K edge of Zn in this compound could not be found in the literature. When the K-absorption edge of S is lined up with the lower edge of the continuum given by Seitz it is seen that the S $K\beta_1$ line falls nearly seven electron volts above the S $3p$ band. This is the same as the effect observed in CaS and MgS and is explained in the same way. It should be noted that in the S $K\beta$ group, the strongest line is taken to be the S $K\beta_1$ line and that it is accompanied by weaker satellites on the long wave-length side instead of the short wave-length side as in the alkaline earth sulphides. This line structure and intensity relation was observed in zinc blende and wurtzite as well as in pellets pressed from the chemically pure reagent.

To locate the Zn $K\beta_5$ line correctly, the Zn $3p$ band was taken as the origin of the Zn $K\beta_1$ line. The Zn $3p$ level was located relative to the Zn $3d$ band by a combination of x-ray data,[13] without the use of Zn $K\beta_5$, the origin of which is doubtful. The equation used was:

$$M_{IV,V} - M_{II,III} = K\alpha_1 + L\alpha_{1,2} - K\beta_1,$$

the $L\alpha$ wave-length being obtained from the measurements of Tyren.[14] The interval between Zn $3d$ and Zn $3p$ was found to be 76.0 electron volts. When the Zn $K\beta_1$ line is placed in coincidence with the Zn $3p$ band, the $K\beta_5$ line falls at

[11] J. C. McDonald, Phys. Rev. 50, 694 (1936).
[12] J. Valasek, Phys. Rev. 43, 612 (1933).
[13] M. Siegbahn, Spektroskopie der Roentgenstrahlen (1931).
[14] F. Tyren, Archiv f. Mat., Astr. och Fysik 25A, 1 (1936).

S^{--} $3p$ as shown in Fig. 3. This indicates that the Zn $K\beta_5$ line which is usually regarded as due to a "forbidden" or quadrupole transition ($\Delta l = 2$) is due instead to a cross transition of a S^{--} $3p$ electron into a K-shell vacancy in the zinc ion. One can thus understand the relatively low intensity of this line and its anomalous variation with atomic number. The above applies to zinc sulphide and probably to all salts of elements in the iron group. The $K\beta_5$ line has also been observed in the x-ray emission spectrum of metallic zinc, in fact, accompanied by a weak and scarcely resolvable $K\beta_2$ line.[15] These lines show a breadth and lack of symmetry which is characteristic of the conduction band in metals.

Their origin is discussed by Beeman and Friedman[16] in connection with their study of the structure of the K-absorption edges of compounds in the neighborhood of the iron group. They also give excellent reasons against the usual interpretation of $K\beta_5$ as a forbidden or quadrupole transition in those cases where there is conduction band formation in the solid. The present observations give support to a similar interpretation in regard to compounds.

The writer takes this opportunity to thank the Graduate School of the University of Minnesota for its support of this investigation, and to Mr. George Werner for his assistance in the laboratory.

[15] J. A. Bearden and C. H. Shaw, Phys. Rev. 48, 18 (1935).

[16] W. W. Beeman and H. Friedman, Phys. Rev. 56, 392 (1939).

An Accurate Measurement of the Energy Released in the Disintegration of Li⁶ by Protons

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The energy release in the reaction Li⁶(p,α)He³ has been determined by a comparison of the He⁴ range with that of the alpha-particles from Be⁹(p,α)Li⁶. The energy of the latter reaction is accurately known from electrostatic deflection measurements. The determination was carried out in a small, variable air pressure, absorption cell and ionization chamber, both being at the same pressure. The device had high dispersion, 1 mm of range corresponding to about 13 cm Hg. Calibration of the cell was carried out by a method which utilized this high dispersion. The Q value for the reaction was found to be 3.945±0.06 Mev as compared to the previously accepted value due to Neuert of 3.72±0.08. With the new Q value, H³ is found to be unstable against β-decay by either 0.19±0.09 or 0.10±0.1 Mev depending on whether Bainbridge's or Aston's value for the deuterium-helium bracket is used. The mass of He³ is found to be 3.01688±0.00011 mass units.

INTRODUCTION

ONLY three nuclear reactions are known at the present time which lead to the formation of the He³ nucleus. The one most studied has been D²+D²→He³+n¹, and this chiefly through measurement of the neutron energy;[1] the alternative being to measure a 4-mm range.

Another reaction is the recently discovered[2] beta-radioactivity of H³. The third is the reaction Li⁶+H¹→He³+He⁴, which is the subject of this paper. These short range particles were first found by Oliphant, Kinsey, and Rutherford.[3] The best measurement of the energy release hitherto published is that of Neuert,[4] who measured the

[1] T. W. Bonner and W. M. Brubaker, Phys. Rev. 49, 19 (1936); T. W. Bonner, Phys. Rev. 52, 686 (1937) and 53, 711 (1938); E. Baldinger, H. Huber, and H. Staub, Helv. Phys. Acta 11, [3] 245 (1938), and others.

[2] L. Alvarez and R. Cornog, Phys. Rev. 56, 613 (1939) and 57, 248A (1940).

[3] M. L. E. Oliphant, B. B. Kinsey, and Lord Rutherford, Proc. Roy. Soc. 141, 722 (1933).

[4] H. Neuert, Physik. Zeits. 36, 629 (1935).